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Phase-Separation Kinetics in Dynamically Asymmetric Binary Fluids: Viscoelastic Effects in Polymer Solutions[1]

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The strong asymmetry in molecular dynamics between the two components of a binary mixture leads to a strong kinetic coupling between the stress field and the order parameter (concentration), which significantly affects the phase separation. A polymer solution, as a typical example of dynamically asymmetric mixtures, behaves as a gel in the initial stage of phase separation for a deep quench, while it behaves as a simple viscous fluid in the final stage. In the intermediate stage, the relaxational nature of the viscoelastic effect plays an important role in pattern evolution, which violates the self-similarity of the growing pattern. To understand the phenomena a concept of *dynamic symmetry* should be introduced in addition to the static composition symmetry.

KEY WORDS: dynamics; phase separation; polymer solution; spinodal decomposition; viscoelastic effect.

1. INTRODUCTION

Phase separation in both polymer/liquid and polymer/polymer mixtures has so far been believed to be essentially the same as that in classical fluids, including binary liquid mixtures and simple fluids [1]. The viscoelastic effect coming from the entanglement of polymer chains has been thought to be important only in the very initial stage, where the phase-separation time t is shorter than the characteristic viscoelastic time τ_t representing the disentanglement time of a chain [2–5]. This leads to the conclusion that the basic kinetic equations describing phase separation of classical binary fluids are valid for polymer mixtures on time scales longer than τ_t and on spatial scales larger than R_g, where R_g is the radius of gyration of a chain.

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In such a space-time region the polymer system behaves as a viscous fluid and usual phase-separation behavior should be observed. Based on the above physical picture, it has been widely accepted that the topological characteristics of polymers do not cause any essential change in the critical dynamics and the phase-separation kinetics and they simply slow down the dynamics through the large viscosity [2, 4, 5]. The experimental results for the spinodal decomposition of polymer systems have been well described in terms of the theories for ordinary binary fluids (see, e.g., Refs. 6 and 7), which supports the above idea. Thus a polymer system has been regarded as an ideal model system to study the general aspect of phase separation in classical binary fluids, because the large size and slow dynamics of polymers make the experimental studies very easy.

For dynamically asymmetric polymer mixtures, however, the above picture is not necessarily true and we need to consider a new effect of viscoelasticity on phase separation. We have recently found experimental evidence that viscoelastic effects severely affect spinodal decomposition and critical phenomena in polymer solutions [8–10, 12]. We propose a new concept of *dynamic asymmetry* and consider how the slow molecular dynamics of a component (polymer) affects the phase-separation kinetics for unstable states [9, 10, 12].

2. EFFECTS OF DYNAMIC ASYMMETRY IN POLYMER SYSTEMS: VISCOELASTIC EFFECTS

It is well known that entangled polymer solutions behave like elastic gels when the characteristic deformation time is shorter than the characteristic rheological time τ_t, while they behave like viscous fluids for slower deformation [2, 13]. This characteristics of polymers has recently attracted much attention, as related to the shear effects on phase separation [14–16]. However, there have been few studies of intrinsic viscoelastic effects [9–12] on phase separation in the absence of an external shear field. We like to raise the following questions: how is spinodal decomposition affected by the viscoelastic properties and how does slow molecular dynamics compete with critical dynamics? All previous theories on phase separation assume that the elementary molecular dynamics is much faster than the critical dynamics, so that the diffusion process is the limiting process. This is the fundamental concept of *dynamic universality*. However, this assumption could be violated by the asymmetry in molecular dynamics between the two components, which could be caused by the slow dynamics of one of the components. Such slow dynamics could originate from either *complex internal degrees of freedom as in polymers*, or *glass-transition phenomena* as shown in Fig. 1. Most previous theories on phase-separation dynamics

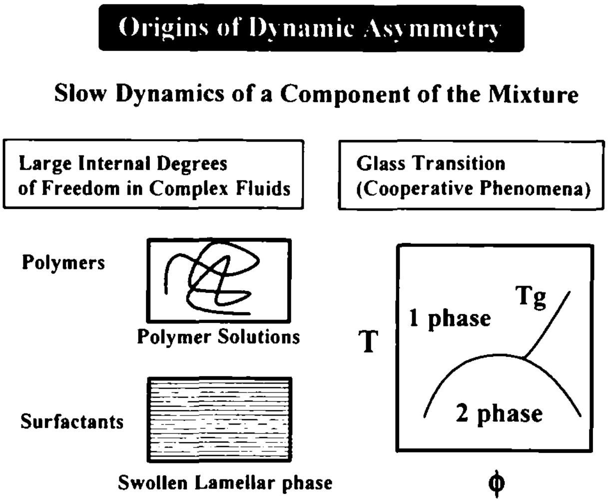

Fig. 1. Typical examples of dynamically asymmetric systems. (i) The slow dynamics in complex fluids originates from the large internal degrees of freedom. (ii) The slow dynamics in mixtures one of whose components is close to the glass transition T_g comes from slow cooperative local motion unique to the glass transition. For both cases, the long-range nature of the geometrical interactions causes the slow dynamics.

assume symmetry in both composition and molecular size. For *dynamically symmetric* cases, the deformation rate of domains is always slower than τ_t of the homogeneous mixture except for the regime when time t is smaller than τ_t. Thus there is no significant viscoelastic effect on phase separation and this has been well established by previous experimental and theoretical studies.

For *dynamically asymmetric cases*, on the other hand, there is a large difference in dynamics between the two coexisting phases, especially for a deep quench. The viscoelastic effect is thus expected to play a dominant role in coarsening. An extreme case of *dynamic asymmetry* is a polymer solution. However, this problem has so far been explored neither theoretically nor experimentally. The probable reason is that most experimental studies on polymer solutions [7] have been restricted to experimental conditions producing only a weak dynamic asymmetry, which are characterized by shallow temperature quenches and by rather low molecular weights of polymers ($M_w < 2 \times 10^5$).

3. ELASTIC EFFECTS IN GELS AND VISCOELASTIC EFFECTS IN POLYMER SOLUTIONS

Here we discuss the specific features of viscoelastic spinodal decomposition, focusing on the similarity and dissimilarity between *elastic spinodal decomposition in gels* [17] and *viscoelastic spinodal decomposition in polymer solutions* [9–12]. A chemical gel has a permanent network of polymer chains which is filled with solvent [18]. Polymer solutions, on the other hand, could have a transient network. The components of both systems have very different dynamic properties: an elastic or transient network characterized by slow dynamics and a fluid characterized by fast dynamics. Thus they have *intrinsic dynamic asymmetry*. It is much easier to understand phase separation in gels than that in polymer solutions, although even the former has been largely unexplored [17]. The reasons are as follows: Elastic effects in gels are energetic effects and can be straightforwardly included in the Hamiltonian. Viscoelastic effects in polymer solutions, on the other hand, are kinetic effects. Thus we cannot include it in the Hamiltonian and need the dynamic equations to describe them. In the following we compare phase separation in polymer solutions with that in gels.

In the initial stage of phase separation, there could be a large difference between gels and polymer solutions. A gel could behave as an elastic body and the elastic effect plays a dominant role even in the beginning of phase separation. Elastic effects might suppress the linear enhancement of concentration fluctuations, which is characteristic of the initial stage of usual spinodal decomposition. Polymer solutions, on the other hand, likely behave as fluids until the dynamic asymmetry between the two phases becomes strong enough to cause the viscoelastic effects. For polymer solutions usual spinodal decomposition probably proceeds for a while. Once the viscoelastic effect starts to play a role, however, it enters into the quasielastic gel-like regime.

In the intermediate stage, both gels and polymer solutions are largely affected by elastic effects. In this regime, the viscoelastic effects in polymer solutions can be regarded as elastic effects. Elastic effects prevent usual spinodal decomposition which is free from any energy barrier. The system must overcome the elastic energy barrier so that phase separation can proceed, since the elastic interaction is directly coupled with concentration fluctuation and the enhancement of concentration fluctuations should always accompany the deformation of the elastic network. This is likely a very unique feature of the quasielastic regime of phase separation common to both gels and polymer solutions. Hence, we have never seen the typical morphologies of usual spinodal decomposition which are characteristic of concentration-fluctuation enhancement without any energetic barrier.

Instead, the phase separation on a large scale proceeds by nucleation and growth of less elastic phases even for unstable states, which seems to be general for elastic spinodal decomposition. After the nucleation of less elastic phases, the concentration changes continuously to the final equilibrium value. This leads to the unusual behavior that the concentration keeps changing significantly even after the formation of the sharp interface. This is in contrast with the common sense view in phase separation of classical binary fluids that the concentration reaches the final equilibrium value after the formation of the sharp interface.

Although the viscoelastic effect looks similar to the elastic effect in the above intermediate stage, there is an essential difference between the two, which becomes evident in the final stage. The former is a kinetic effect, while the latter is a static, energetic effect. This leads to the difference in the very late stage morphology between elastic and viscoelastic spinodal decomposition: The elastic effects affect the morphology even in the late stage. The viscoelastic effects, on the other hand, do not affect the final morphology, which is purely determined by energetic factors such as interfacial energy, since there remain only viscous effects and no elastic effects for $t \to \infty$. This relaxational nature of viscoelastic effects violates the self-similar coarsening of the pattern. Such behavior was experimentally observed as shown in Figs. 3b and 3c in Ref. 11.

In viscoelastic spinodal decomposition, even for the mixture rich in a less viscoelastic component, the more viscoelastic phase tends to become the continuous matrix phase during the crossover from the regime dominated by the dynamic symmetry to the regime dominated by the static symmetry. This is likely due to the fact that (i) a relaxational nature of the viscoelastic effect causes the continuous change of the apparent phase diagram and leads to the formation of network-like pattern, and (ii) the connectivity of the phase is preserved till the late stage since the stress is always supported by polymer-rich phases and thus the polymer-rich phase is selectively deformed to keep the stress balance. It should be noted that a similar sponge-like pattern has first been observed by Sekimoto *et al.* [17] in the numerical simulation of volume phase transition in gel (see the discussion there).

4. VISCOELASTIC SPINODAL DECOMPOSITION: DYNAMIC PHASE DIAGRAM

In Fig. 2, we propose a new, nonthermodynamic phase diagram including the dynamic effect. For a deep quench there are two lines related to the symmetry [10, 11]. One is the usual static, composition symmetry line (SSL) and the other is a dynamic symmetry line (DSL). The latter is related to the dynamic asymmetry. In the following we focus our attention mainly on deep quenches. For a shallow quench the dynamic asymmetry is so weak that nothing unusual happens except for the very initial stage ($t < \tau_t$) where the viscoelastic effect could be important. Thus the phase-separation behavior ($t > \tau_t$) is expected to be similar to that of binary liquid mixtures for a shallow quench, as studied by many researchers [7]. Next we consider unusual viscoelastic phase separation of a polymer solution under a deep quench (see Fig. 2). When we quench the system into the region at the left side of DSL, the polymer-rich phase appears as droplets in the initial stage of phase separation. We call this phase a *moving droplet phase* (MDP), since this polymer-rich droplet moves vigorously by Brownian motion. We call this region of the phase diagram the *MDP region*. In the region between DSL and SSL, the solvent-rich droplet is observed in the initial stage, but the polymer-rich matrix transforms into a network-like

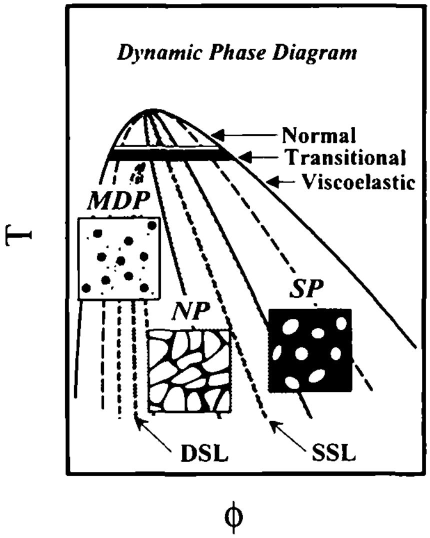

Fig. 2. Schematic phase diagram including the dynamic effect. Here both the composition symmetry line (SSL) and the dynamic symmetry line (DSL) are drawn. For deep quenches, we see viscoelastic spinodal decomposition: (1) a moving droplet phase (MDP) in the left side of DSL, (2) a network-like phase separation (NP) between DSL and SSL, and (3) a sponge-like phase separation (SP) in the right side of SSL. For quenches with intermediate depths, there is a gradual transitional region from normal to viscoelastic phase separation.

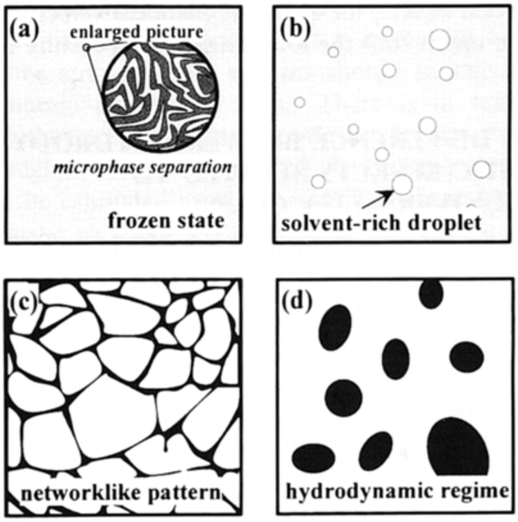

Fig. 3. Typical coarsening process of the network-like phase (NP) during viscoelastic spinodal decomposition. The schematic figures express the time evolution of the phase-separated pattern. The increase in the darkness of the hatched regions expresses the increase in the concentration of polymer with time. The frozen state (a) has the inhomogeneous structure with small spatial scale, which is caused by the normal phase separation in the initial stage. In the initial stage the coarsening is dominated by the viscoelastic energy, while in the final process the domain shape is determined by the interfacial energy as in usual phase separation of binary fluids and becomes spherical (d).

pattern (NP), and finally transforms into a droplet pattern of the polymer-rich phase. Thus we call this region the *NP region*. The phase-separation behavior in the *NP region* is schematically drawn in Fig. 3. On the right side of SSL, the solvent-rich phase always forms droplets and the phase-separation pattern becomes a sponge-like pattern (SP). Thus we call this region the *SP region*. The transition from normal phase separation to viscoelastic phase separation is not sharp and there is a gradual transitional region between them.

Although it is well known that the external shear field shifts the apparent phase diagram and strongly affects spinodal decomposition [19, 14–16], this kind of viscoelastic effect due to the self-induced, internal velocity field has never been considered, and further theoretical studies are necessary to clarify the effect and to establish this concept. There are many possibilities for new effects; for example, the local velocity field induced by phase separation might shift the local critical temperature during the phase separation.

5. ESSENTIAL DIFFERENCE BETWEEN HYDRODYNAMIC AND VISCOELASTIC EFFECTS RELATED TO DYNAMIC UNIVERSALITY CLASS

Here we compare the hydrodynamic and viscoelastic effects on critical dynamics, focusing on what kinds of effects lead to the formation of a new dynamic universality class. It is widely accepted that critical phenomena cannot be classified solely by the types of Hamiltonians and order parameters. The hydrodynamic interaction in binary fluids is one of the most well-known kinetic effects. In the case of hydrodynamic interactions, there are no spatial and temporal scales characterizing its effect. This is probably the reason why this interaction leads to the formation of the new dynamic universality class, *model H* [1]. Similar to this hydrodynamic effect, the viscoelastic effect never appears in the Hamiltonian, while it appears only in the kinetic equations. In the case of viscoelastic effects, however, there is an intrinsic characteristic time scale (τ_t) for it, and thus, in the limit of $T \rightarrow T_c$ (T is the temperature, T_c the critical temperature), where $\tau_\xi \gg \tau_t$ (τ_ξ is a characteristic time scale of concentration fluctuation), the critical dynamics can be free from this effect at least theoretically. Thus the final stage of spinodal decomposition should also be free from the viscoelastic effect. If we formally classify the dynamic universality class by the behavior in the limit of $T \rightarrow T_c$, we should probably say that polymer mixtures with dynamic asymmetry belong to the same dynamic universality class (*model H*) as classical fluids with dynamic symmetry. However, if we take the limit of $N \rightarrow \infty$ (N is the degree of polymerization), we cannot neglect the dynamic asymmetry effect even near the critical point. In the actual experiments, further, the system could apparently behave differently from the prediction of *model H* especially for large N. To settle this delicate problem, further theoretical and experimental studies are necessary. This problem could also be related to the question of how to understand the competition between critical effects near T_c and tricritical effects near the θ point.

6. SUMMARY

It is found that critical phenomena in polymer mixtures having *dynamic asymmetry* (such as polymer solutions) are strongly affected by the viscoelastic effect for both stable and unstable states. Although it has so far been believed that the dynamic universality class of polymer systems is the same as that of binary fluid systems (*model H* in the Hohenberg–Halperin notation [1]), we have demonstrated that it might not be true, and that dynamically asymmetric polymer systems should practically be classified into a new dynamic universality class. There is at least the dynamic crossover from the nonuniversal viscoelastic regime to the universal hydrodynamic regime in the vicinity of T_c and the dynamic crossover temperature can be estimated as $T - T_c \sim N^{\beta} T_c$, where $1/2 < \beta \leqslant 1$.

For *viscoelastic spinodal decomposition*, the simple scaling scheme breaks down because of the temporal change in the strength of the viscoelastic effect which reflects the decay of the deformation rate with coarsening (viscoelastic relaxation). These kinetic effects do not affect the final equilibrium state, which is determined by the static Hamiltonian. Further experimental studies in both metastable and unstable states and deeper theoretical understanding of the phenomena based on the dynamic equations derived by Doi and Onuki [15] are highly desirable.

These phenomena are expected to be universal in any system having an asymmetry in elementary molecular dynamics. The possible candidates for *dynamic asymmetry* are (1) slow dynamics in complex fluids such as polymer solutions and surfactant solutions, due to their complex internal degrees of freedom (e.g., entanglement effects in polymers), and (2) slow dynamics near a glass transition (see Fig. 1).

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